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# THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING

Research and Advanced Technology Division

UNITED TECHNOLOGY CORPORATION  
A Subsidiary of United Aircraft Corporation  
P.O. BOX 358  
Sunnyvale, California

SIXTH QUARTERLY TECHNICAL SUMMARY REPORT  
1 JUNE THROUGH 31 AUGUST 1962  
CONTRACT No. Nonr 3433(00)

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SIXTH QUARTERLY TECHNICAL SUMMARY REPORT  
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Under Contract No. Nonr 3433(00)

Propulsion Chemistry Branch  
Material Sciences Division  
Office of Naval Research

ARPA ORDER NO. 184-62

(This project is financially supported by the  
Advanced Research Projects Agency)

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## ABSTRACT

Infrared spectra of nitryl fluoride, which are free of nitrogen dioxide absorption peaks, have been obtained by the addition of excess fluorine to the product in the infrared cell. An apparent equilibrium dissociation of nitryl fluoride into nitrogen dioxide and fluorine exists which normally leads to partial decomposition of  $\text{NO}_2\text{F}$ .

Preliminary calorimetric determinations of the heat evolved during formation of fluorine perchlorate by fluorination of 70 percent perchloric acid have yielded an approximate value for the heat of formation of fluorine perchlorate of +0.69 Kcal/mole.

Detailed studies of the synthesis of trifluoromethyl hypofluorite, fluorine fluorosulfonate, and pentafluorosulfur hypofluorite have been conducted to establish optimum reaction conditions. Material of high purity has been obtained; however, further purification will be required for pentafluoro-sulfur hypofluorite, which was isolated at approximately 90 percent purity.

Several reactions have been evaluated to determine their suitability for the calorimetric evaluation of their heat of reaction with fluorine nitrate. None has been found to be completely satisfactory, and additional reactions are being considered. Similarly,  $\text{CF}_3\text{OF}$ ,  $\text{FSO}_3\text{F}$ , and  $\text{F}_5\text{SOF}$  have been found to be unreactive with hydrogen, and since the synthesis reactions are also unsatisfactory for calorimetry studies, other reactions are being screened for suitability.

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## 1.0 INTRODUCTION

This report is the Sixth Quarterly Technical Summary Report issued in partial fulfillment of Contract Nonr 3433(00). This report covers the work accomplished during the months of June, July, and August, 1962.

## 2.0 OBJECTIVES

The objective of the current program is an evaluation of the O-F bond energy in compounds exhibiting well-defined O-F bonding. Previous studies have established by measurements with a flow calorimeter that the heat of formation of  $\text{NO}_3\text{F}$  is +2.5 Kcal/mole. Auxillary studies have been made to evaluate the heat of formation of  $\text{NO}_2\text{F}$ , a compound containing N-F bonding. A preliminary heat of formation of -19 Kcal/mole has been obtained for  $\text{NO}_2\text{F}$ ; however, this value is uncertain.

The specific objectives of the research effort conducted during the present report period have been as follows:

- A. An investigation leading to the preparation of high purity  $\text{NO}_2\text{F}$ , preparatory to defining a more precise value for the heat of formation
- B. A further screening of reactions of  $\text{NO}_3\text{F}$  suitable for calorimetric determination of heat of reactions to corroborate the heat of formation derived earlier from the synthesis reaction
- C. Measurement of the heat of formation of  $\text{ClO}_4\text{F}$  by direct synthesis in a flow calorimeter
- D. Completion of a detailed study of the synthesis of additional O-F bonded materials including  $\text{F}_5\text{SOF}$ ,  $\text{FSO}_3\text{F}$ , and  $\text{CF}_3\text{OF}$  to determine optimum synthesis conditions
- E. Development of analytical procedures for the accurate analysis of reaction products obtained in the synthesis of hypofluorite materials.

### 3.0 TECHNICAL ACTIVITY

#### 3.1 STUDY OF $\text{NO}_2\text{F}$

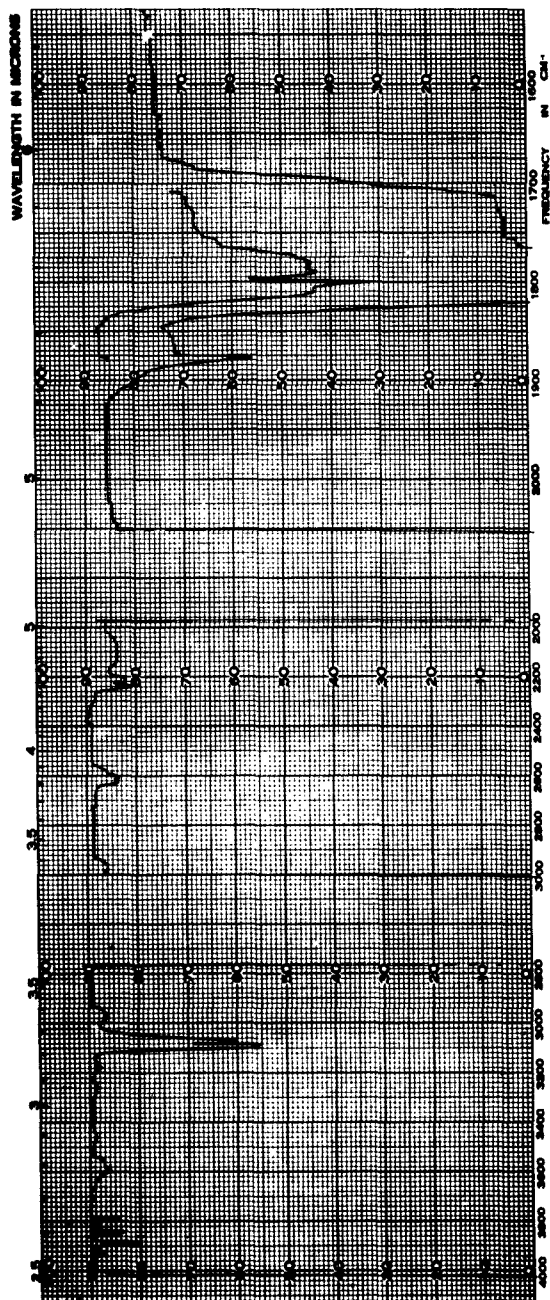
Nitryl fluoride of high purity has been prepared and infrared spectra have been obtained which truly reflect the purity of the product. Spectra previously obtained have shown a high concentration of  $\text{NO}_2$  in nitryl fluoride, in agreement with published information on the spectrum of nitryl fluoride\* in that a spectrum could not be obtained free of this impurity. This is apparently caused by partial decomposition of the material with an equilibrium being established between the product, nitrogen dioxide, and fluorine. Calculations based on the heat of formation of  $\text{NO}_2\text{F}$  as derived earlier, and other available thermodynamic data\*\* indicate that at room temperature nitryl fluoride would be considerably dissociated into these products. During this report period, spectra have been obtained free of nitrogen dioxide absorption peaks. Nitryl fluoride was prepared in an all-glass system from the reaction of sodium nitrite and fluorine by the method of Hetherington and Robinson.\*\*\* The product was transferred to a 10 cm path-length Kel-F infrared cell with sodium chloride windows, and an excess of fluorine was admitted immediately to retard formation of nitrogen dioxide. In this manner, spectra of nitryl fluoride as shown in

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\* Dodd, R. E., J. A. Rolfe, and L. A. Woodward, Trans. Faraday Soc. 52, 145-151, 1956.

\*\* JANAF, Interim Thermochemical Tables, The Dow Chemical Co., 1960.

\*\*\* Hetherington, G. and P. L. Robinson, Chemical Society Special Publication No. 10, 23-32, 1957.



SAMPLE 93-CF-125  
 C<sub>12</sub>H<sub>18</sub>F<sub>2</sub>  
 2nd Sample Unmanned  
 PVT (17) mm  
 SOLVENT None  
 DRYING Force  
 REFERENCE None  
 SOLVENT None  
 DATE 1-6-64  
 TIME 10:30 AM  
 BY J. H. HARRIS  
 J. H. HARRIS  
 Beckman  
 MODEL 107

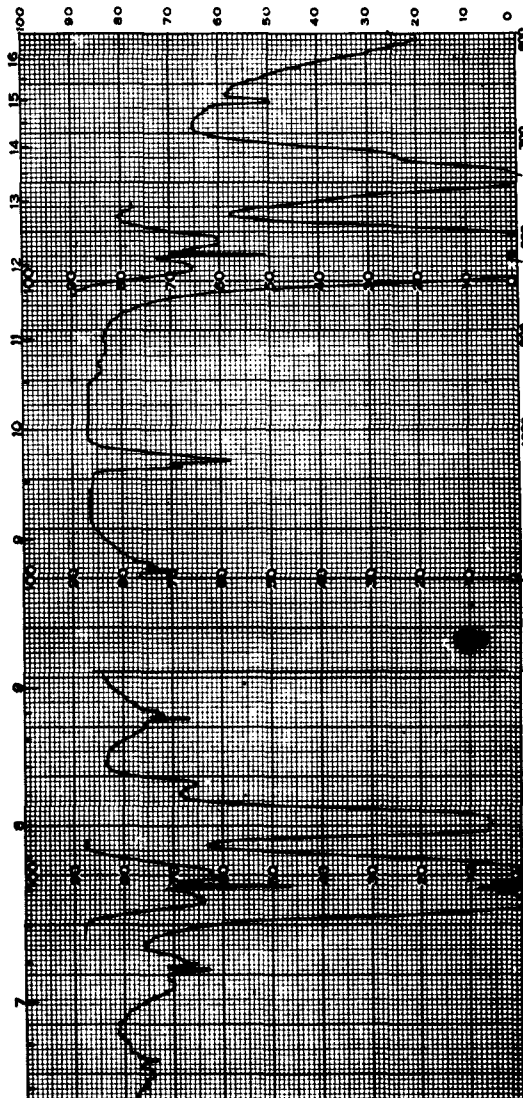


FIGURE 1. INFRARED SPECTRUM OF NO<sub>2</sub>F

Figure 1, have been obtained without the absorption of nitrogen dioxide. Hydrogen fluoride, silicon tetrafluoride, dinitrogen pentoxide, and possibly a nitryl fluoride-hydrogen fluoride complex (at 1805-1810  $\text{cm}^{-1}$ ) were noted as impurities.

### 3.2 STUDY OF $\text{NO}_3\text{F}$

As previously reported\*, hydrogen appeared to be unreactive with fluorine nitrate; therefore, an investigation of other gaseous fuels was inaugurated to evaluate the applicability of other combustion reactions to calorimetric study. Fuels were selected on the basis of their expected ease of oxidation to relatively simple and easily identifiable gaseous products. Those fuels which would lead to the formation of solid products were generally not considered because of the difficulties anticipated in their analysis when contaminated with the passivation coating from the walls of the combustion calorimeter.

Studies were made by charging a weighed amount of fluorine nitrate into one portion of the two-cylinder calorimeter and allowing it to mix with a known amount of fuel in the other arm by remotely opening the connecting valve. If no spontaneous reaction appeared to occur on mixing, a spark was applied to the system. Where applicable, pressure measurements were made to establish the extent of reaction. Infrared analysis of the resulting gas mixture was used to identify any reaction products, and the weight of any solid materials formed was obtained by weighing the evacuated combustion calorimeter.

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\* Breazeale, J. "Thermochemistry of Oxygen-Fluorine Bonding," Quarterly Technical Summary Report No. 5, 2002-QT5, Contract Nonr 3433(00), United Technology Corporation, May 1962.

Reactions of  $\text{NO}_3\text{F}$  were attempted with  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{BF}_3$ .  $\text{NO}_3\text{F}$  reacted hypergolically with  $\text{NH}_3$ ,  $\text{NO}$ , and  $\text{H}_2\text{S}$  and partially, after spark initiation, with  $\text{HCl}$ ,  $\text{CO}$ , and  $\text{BF}_3$ . No reaction could be induced in a  $\text{NO}_3\text{F}$  -  $\text{CH}_4$  mixture.

A varying distribution of products was noted in reactions of  $\text{NO}_3\text{F}$  with  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{BF}_3$ ,  $\text{HCl}$ , and  $\text{CO}$ . Both gaseous and solid products were obtained with  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{BF}_3$ , while  $\text{HCl}$  and  $\text{CO}$  gave only gaseous products. These results limit the utility of these reactions for calorimetric studies.

The reaction between  $\text{NO}_3\text{F}$  and  $\text{NO}$  gave the most promising results from a calorimetric standpoint because of the formation of only a small amount of solid product and a comparatively clean, reproducible infrared spectrum of gaseous products. However, since some reaction occurred between the products and the cell windows, further effort is required to define the complete reaction more clearly.

Attempts were made to catalyze a reaction between  $\text{NO}_3\text{F}$  and  $\text{H}_2$  by (1) the use of a platinum wire fuse to serve as a hydrogenation catalyst as a replacement for nichrome fuse and (2) addition of a small quantity of  $\text{O}_2$  to the  $\text{NO}_3\text{F}$  to initiate reaction with the excess hydrogen. Neither experiment gave any indication of a reaction of the  $\text{NO}_3\text{F}$  with the fuel.

### 3.3 STUDY OF $\text{ClO}_4\text{F}$

#### 3.3.1 Combustion Calorimetry Experiments

Studies were conducted to determine the suitability of hydrogen as a fuel for fluorine perchlorate. However, as with  $\text{NO}_3\text{F}$ , fluorine perchlorate and hydrogen were neither hypergolic nor reactive when spark ignition was attempted. Infrared analyses showed the presence of only fluorine perchlorate in several experiments although the concentration and ratio of the reactants were varied. Pure fluorine perchlorate has been found to be spark-sensitive, decomposing to

chlorine dioxide and possibly chlorine monofluoride. Because fluorine perchlorate contains two halogens, reactions of the type attempted with fluorine nitrate are expected to give an even wider variety of products and are, therefore, less attractive for calorimetric studies.

### 3.3.2 Synthesis Calorimetry Experiments

In an initial attempt to prepare fluorine perchlorate by reaction of fluorine with 70 per cent perchloric acid in the Teflon-coated calorimeter described earlier\*, three side products were found to be present by fractional codistillation with a low over-all yield of fluorine perchlorate. On the basis that the impurities were introduced by reaction of perchloric acid with the stainless steel components of the calorimeter and subsequent fluorination of these products, the portions of the dip spouts which extended into the perchloric acid solution were replaced with Teflon capillary tubing. In two subsequent experiments, conversions to  $\text{ClO}_4\text{F}$  of less than three per cent were obtained, a consequence of the small amount of perchloric acid contained in the reactor resulting in a short fluorine-perchloric acid contact time.

In an attempt to improve the percentage yield of fluorine perchlorate for short reaction times, preparations were attempted using a Kel-F reactor employed in the initial synthesis studies of fluorine perchlorate. The reactor, which increases fluorine-perchloric acid contact by means of an extended Kel-F side arm and Kel-F packing in the reactor body, contains five times as much perchloric acid solution

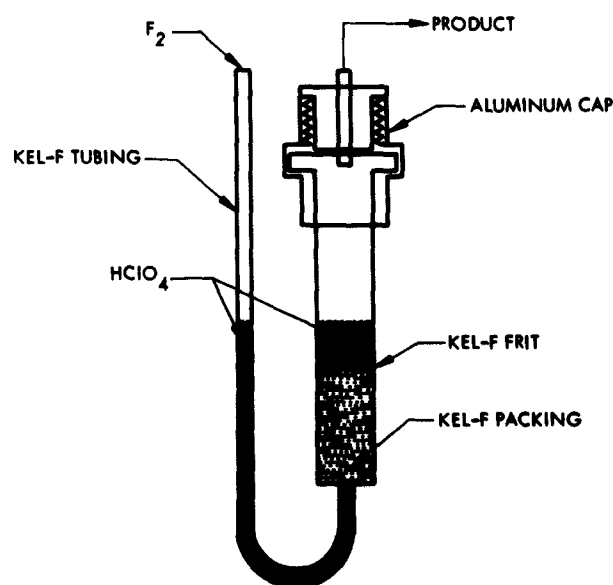
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\* Breazeale, J., op. cit.



as the dipspout reactor. A sketch of the apparatus is shown in Figure 2. The product obtained in the first three calorimetric studies using the new reactor exploded before a measurement could be taken, but was collected successfully in the fourth and fifth runs, yielding fluorine perchlorate of increased yield and purity, as shown in Table I.

A preliminary determination of the heat of formation of fluorine perchlorate was made from the successful experiments. However, there is considerable uncertainty in the results owing to both the poor heat transfer characteristics of Kel-F with a resultant long equilibration period following reaction, and the large heat capacity of the system owing to the quantity of water required to cover the apparatus. Therefore, the heat of formation value of +0.69 Kcal/mole, derived from the graph shown in Figure 3, must be considered as only preliminary.



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FIGURE 2. FLUORINE PERCHLORATE SYNTHESIS CALORIMETER

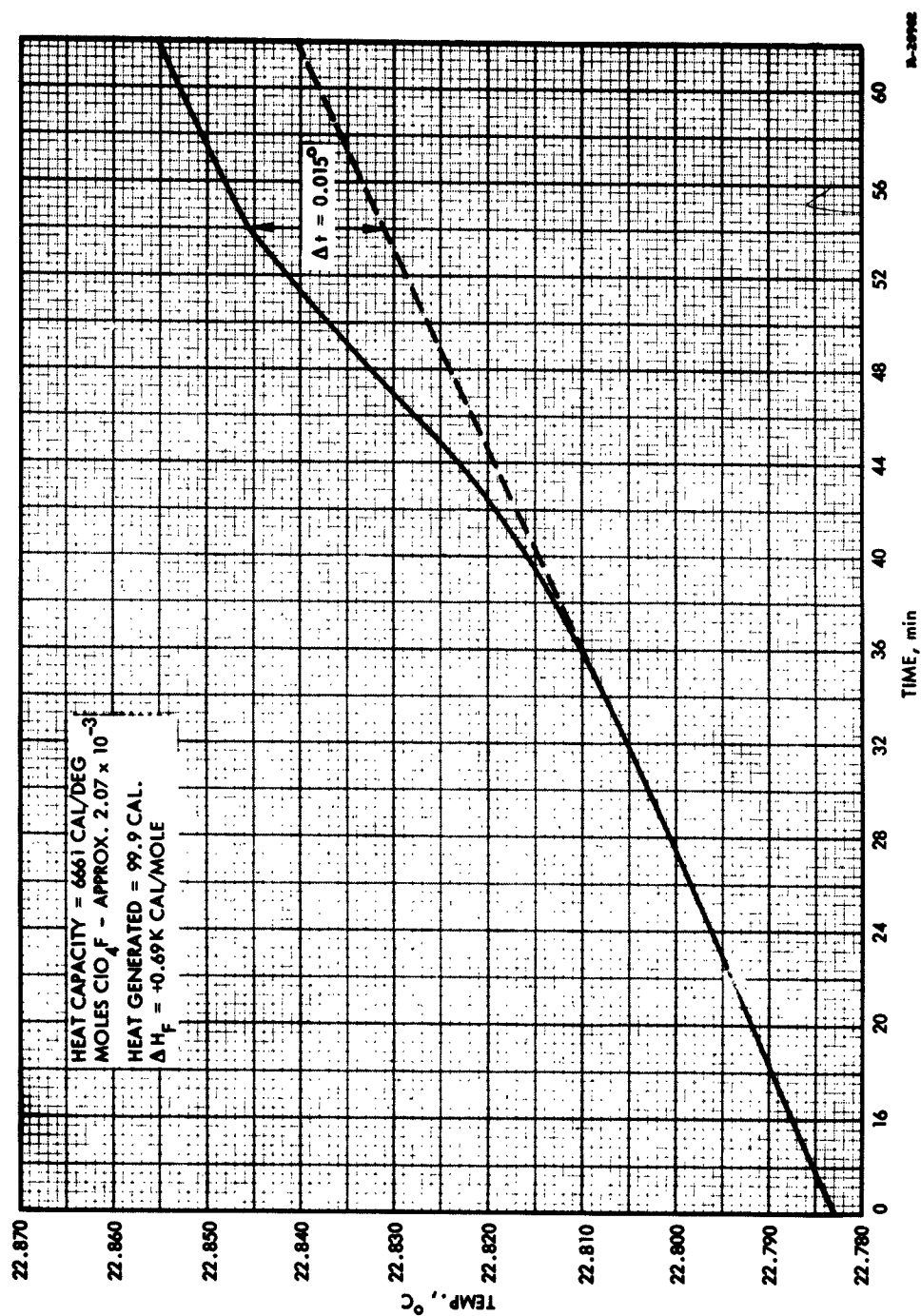
FIGURE 3. CALORIMETRIC DATA: REACTION OF  $\text{F}_2$  AND  $\text{HClO}_4(70\%)$

TABLE I  
REACTION OF  $F_2$  AND  $HClO_4$ (70%)

RUN NO.	1	2	3	4	5
$F_2$ , mmoles	20.0	8.42	6.84	7.64	7.64
$HClO_4$ , mmoles	296.5	296.5	296.5	296.5	296.5
Reaction Time, min.	30.0	25.0	20.0	20.0	20.0
$F_2$ flow rate, mmoles/min.	0.67	0.34	0.34	0.38	0.38
Comments	Product ex- ploded in liq. $O_2$ Trap	Product exploded while warming	Product ex- ploded while warming		
Percent yield	- -	- -	- -	24	28
I. R. analysis	- -	- -	- -	only $ClO_4F$	only $ClO_4F$

### 3.4 STUDY OF $CF_3OF$

#### 3.4.1 Synthesis and Purification of Trifluoromethyl Hypofluorite

The method of preparation and purification of trifluoromethyl hypofluorite has been reported previously.\* The work on this compound during the present report period has involved attempts to establish the quantitative reactions occurring upon hydrolysis in order to apply this system to calorimetric study. The results of chemical analysis of hydrolyzed samples of  $CF_3OF$  as shown in Table II do

\* Breazeale, J., op. cit.

not agree with the theoretical composition of purified  $\text{CF}_3\text{OF}$  within the limits necessary for calorimetric evaluation.

TABLE II  
CHEMICAL ANALYSIS OF TRIFLUOROMETHYL HYPOFLUORITE

	Carbon percent	Fluorine percent	Base Consumed mmoles/g
Theoretical	11.5	73.1	57.7
Hydrolysis #1	10.2	67.3	54.2
Hydrolysis #2	11.0	67.5	54.8
Hydrolysis #3	6.6	66.3	36.8
Hydrolysis #4	11.4	66.2	54.0

Infrared analysis of the material hydrolyzed indicated that it consisted of trifluoromethyl hypofluorite with a very small amount of carbonyl fluoride. Consequently, the percent carbon would be expected to be slightly greater and the percent fluorine slightly less than theoretical for pure trifluoromethyl hypofluorite; however, the results show that both carbon and fluorine analyses are less than theoretical. The method of hydrolysis and chemical procedures of analysis are being re-examined.

#### 3.4.2 Combustion Calorimetry Experiments

An investigation of reactions of  $\text{CF}_3\text{OF}$ , such as combustion with hydrogen or simple decomposition, was initiated to evaluate their suitability for calorimetric studies. Although varying pressures

and ratios of  $H_2$  and  $CF_3OF$  were employed, initiation of a reaction could not be accomplished by spark ignition. Infrared spectra analysis did not reveal formation of any new compounds after sparking. These results corroborate a report by Cady\* that trifluoromethyl hypofluorite and hydrogen do not interact until a temperature of  $160^\circ C$  is reached.

No decomposition of trifluoromethyl hypofluorite was detected upon sparking the gas with a hot wire and Tesla coil in the combustion calorimeter. This result is consistent with the observation by Cady\*\* that no decomposition of trifluoromethyl hypofluorite was noted until the gas had been continuously sparked for twenty-four hours.

### 3.5 STUDY OF $FSO_3F$

#### 3.5.1 Synthesis and Purification of Fluorine Fluorosulfonate

As reported previously,\*\*\* the two major products of the reaction of fluorine and sulfur trioxide at  $220^\circ C$  in the catalytic reactor are sulfuryl fluoride and fluorine fluorosulfonate. It has been found that vacuum distillation of the crude product removes the more volatile sulfuryl fluoride and results in fluorine fluorosulfonate of high purity, as determined by thermal conductivity measurements on the products separated by fractional codistillation. The infrared spectrum of the fractionally codistilled material indicated the only

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\* Cady, G. H., J. Am. Chem. Soc., 70, 3986, 1948.

\*\* Cady, G. H., J. Am. Chem. Soc., 79, 5628, 1957.

\*\*\* Breazeale, J., op. cit.

impurity to be silicon tetrafluoride. In an effort to remove the silicon tetrafluoride from the product, all glass was removed from the system. The sulfur trioxide was contained in a stainless steel trap fabricated from a Hoke cylinder and the flowrator was replaced by a calibrated stainless steel valve with micrometer head. The infrared spectrum of the product obtained with this apparatus showed the absence of silicon tetrafluoride.

Two samples of the product from the vacuum distillation were hydrolyzed and analyzed for fluorine and sulfur. The results are summarized in Table III.

TABLE III  
CHEMICAL ANALYSIS OF FLUORINE FLUOROSULFONATE

	Sulfur percent	Fluorine percent	Base Consumed mmoles/g
Theoretical	27.2	32.2	33.9
Hydrolysis #1	26.3	33.8	36.0
Hydrolysis #2	38.2	32.2	29.1

The results of the first hydrolysis corresponds to a 97 percent fluorine fluorosulfonate-3 percent silicon tetrafluoride mixture. In the second hydrolysis the theoretical result was obtained for the fluorine, but the sulfur analysis was quite high. The sulfate precipitate appeared green in color and was presumably contaminated.

### 3.5.2 Combustion Calorimetry Experiments

The suitability of hydrogen as a fuel for  $\text{FSO}_3\text{F}$  was investigated for potential application in calorimetry studies. However, fluorine fluorosulfonate and hydrogen were not hypergolic nor reactive when spark ignition was attempted. Infrared analyses did not indicate the presence of any new materials nor was any thermal effect noted in the several experiments conducted. The concentration of hydrogen and the ratio of reactants was varied without effect.

### 3.6 STUDIES OF $\text{F}_5\text{SOF}$

Several reactions to produce pentafluorosulfur hypofluorite from thionyl fluoride and fluorine at approximately  $220^\circ\text{C}$  have been conducted by the procedure of Dudley, Cady, and Eggers.\* The thionyl fluoride was prepared from thionyl chloride and antimony trifluoride using antimony pentachloride as catalyst according to the method of Smith and Muetterties.\*\* Fractional codistillation of the pentafluorosulfur hypofluorite product followed by infrared analysis of the various fractions has indicated that usually three to five products are produced: pentafluorosulfur hypofluorite, thionyl tetrafluoride, sulfuryl fluoride, sulfur hexafluoride, and silicon tetrafluoride.

Attempts were made to purify the product obtained from three of these reactions by vacuum distillation of the impurities which are all more volatile than the hypofluorite. The degree of purity obtained was

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\* Dudley, F. B., G. H. Cady, and D. F. Eggers Jr., J. Am. Chem. Soc.; 78, 1553-1556, 1956.

\*\* Smith, W. C. and E. L. Muetterties, (ed. E. G. Rochow), Inorganic Syntheses (New York: McGraw-Hill Book Co., 1960), Vol. IV, pp. 162-163.

determined by passing the purified product through the fractional co-distillation column. Material containing 87, 90, and 92.7 percent pentafluorosulfur hypofluorite, or a total of six grams of approximately 90 percent purity, was obtained and will be used for preliminary combustion and hydrolysis studies.



#### 4.0 FUTURE WORK

Additional effort will be expended in synthesis and purification of samples of trifluoromethyl hypofluorite, fluorine fluorosulfonate, and pentafluorosulfur hypofluorite for calorimetric investigation. Consistent and accurate analytical data will be obtained to establish the compositions of the samples employed in the calorimetric studies.

The heat of formation of fluorine perchlorate will be studied by additional measurements of the heat of reaction between fluorine and perchloric acid in the modified flow calorimetric reactor.

Experiments will be conducted to establish a more precise value for the heat of formation of nitryl fluoride from a study of its equilibrium dissociation reaction as a function of temperature.

Because the synthesis reactions for trifluoromethyl hypofluorite, fluorine fluorosulfonate, and pentafluorosulfur hypofluorite are conducted at high temperatures, they are not easily adaptable to calorimetric evaluation. Therefore, other reactions, including hydrolysis, will be investigated to evaluate their applicability for this use. Similarly, additional reactions will be considered to corroborate the heats of formation inferred for fluorine perchlorate and fluorine nitrate from their synthesis reactions.